Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

Quarterly Technical Progress Report

January 1, 2005 – March 31, 2005

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ABSTRACT

This document summarizes progress on Cooperative Agreement DE-FC26-01NT41185, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," during the time-period January 1, 2005 through March 31, 2005. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE), and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. Oxidized mercury is removed in the wet FGD absorbers and collected with the byproducts from the FGD system. The current project is testing previously identified catalyst materials at pilot scale to provide engineering data for future full-scale designs. The pilot-scale tests are being conducted for 14 months or longer at each of two sites to provide longer-term catalyst life data.

This is the fourteenth full reporting period for the subject Cooperative Agreement. During this period, only the second pilot unit, at CPS' Spruce Plant, was operated. Operation of the first pilot unit at the GRE Coal Creek site was concluded in 2004. That pilot unit was shipped to TXU Generation Company LP's Monticello Steam Electric Station, for mercury oxidation catalyst testing as part of NETL project DE-FC26-04NT41992.

For the second pilot unit, at Spruce Plant, one catalyst activity measurement trip was conducted in February. These results are discussed briefly in this report. The pilot unit was off line for approximately one month during the quarter, from mid-February through mid-March, due to a scheduled host station outage.

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INTRODUCTION

This document is the quarterly Technical Progress Report for the project "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," for the time-period January 1, 2005 through March 31, 2005. The objective of this project is to demonstrate at pilot scale the use of solid honeycomb catalysts to promote the oxidation of elemental mercury in the flue gas from coal combustion. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-01NT41185. EPRI, Great River Energy (GRE) and City Public Service (CPS) of San Antonio are project co-funders. URS Group is the prime contractor.

The mercury control process under development uses catalyst materials applied to honeycomb substrates to promote the oxidation of elemental mercury in the flue gas from coal-fired power plants that have wet lime or limestone flue gas desulfurization (FGD) systems. The oxidizing species are already present in the flue gas, and may include chlorine, hydrochloric acid (HCl), oxygen and/or other species. Oxidized mercury is removed in the wet FGD absorbers and co-precipitates with and/or adsorbs on the FGD solid byproducts. The objective of this project is to test previously identified catalyst materials at pilot scale to provide engineering data for future full-scale designs. The pilot-scale tests are being conducted for 14 months or longer at each of the two sites to provide longer-term catalyst life data. After completing the project, it is expected that sufficient full-scale test data will be available to design and implement demonstration-scale installations of the catalytic mercury oxidation technology.

The two utility team members are providing co-funding, technical input, and host sites for testing as part of this project. GRE provided the first test site at their Coal Creek Station (CCS), which fires North Dakota lignite, and CPS is providing the second site at their J.K. Spruce Plant, which fires Powder River Basin (PRB) subbituminous coal. These two host sites each have existing wet FGD systems downstream of high-efficiency particulate control devices, an ESP at CCS and a reverse-gas fabric filter (baghouse) at Spruce**.**

Testing has been completed at the first site, but continues at the second site, CPS' Spruce Plant. This progress report discusses results from Spruce during the quarter.

The remainder of this report is divided into five sections: an Executive Summary followed by a section that describes Experimental procedures, then sections for Results and Discussion, Conclusions, and References.

EXECUTIVE SUMMARY

Summary of Progress

The current reporting period, January 1, 2005 through March 31, 2005, is the fourteenth full technical progress reporting period for the project. During this period, there was no testing at the first pilot unit site, at the GRE Coal Creek Station, and no related project efforts. For the second pilot unit at CPS' Spruce Plant, the catalyst pilot unit continued in operation through the quarter, although it was off line for approximately one month due to a host station outage. One catalyst activity measurement trip was conducted, in February.

February catalyst activity results from Spruce showed that the fabric filter outlet flue gas mercury content is still highly oxidized (greater than 90% in some instances). The resulting, relatively low inlet elemental mercury concentrations to the pilot unit (1 $\mu g/Nm^3$ or less in some cases) and significant temporal variations in concentration make it difficult to quantify catalyst oxidation activity. To improve the accuracy of the mercury oxidation measurements, two newer mercury SCEMs with more sensitive atomic absorption detectors were used to simultaneously monitor the pilot inlet and catalyst outlet locations. In spite of this measurement approach, the results from this trip were inconclusive with regards to oxidation catalyst activity for the four catalysts. In some cases, catalyst outlet total and elemental mercury concentrations were measured to be higher than inlet concentrations, which is not an expected result. A number of quality control/quality assurance measures were implemented, including replacing a suspect mercury SCEM with a third unit, switching SCEM units between analyzing the catalyst inlet and outlet locations, and using permanently installed versus temporary sample delivery piping and inertial gas separator (IGS) filter. None of these efforts conclusively improved the apparent quality of the measured mercury concentration data. Because of these measurement anomalies, the data from the February trip are still being reviewed, and a follow up measurement trip is being conducted in April.

Problems Encountered

The only significant problems encountered during the reporting period were the mercury SCEM measurement issues described in Section 4 of this report and mentioned above.

Plans for Next Reporting Period

During the next reporting period (April 1 through June 30, 2005), operation of the second oxidation catalyst pilot unit, at CPS' Spruce Plant, will be concluded. At the same time, end-of-test catalyst activity measurements will be made. A number of in situ catalyst regeneration tests will likely be conducted, depending on which catalysts show measurable loss of activity after the 16 to 17 months they will have been in service at Spruce. After the regeneration tests, the pilot unit will be shipped to Plant Yates for oxidation catalyst testing as part of Cooperative Agreement DE-FC26-04NT41992. Also during the quarter, a Topical Report will be prepared that presents and discusses results from the Spruce Plant testing.

Prospects for Future Progress

The project period of performance will have ended at the end of the previous reporting period (June 30, 2005), so no testing is scheduled at either of the two sites. Both pilot units will have been shut down and moved to new sites as part of the 41992 project. The only remaining project effort will be submittal of the final report.

EXPERIMENTAL

The work described in this technical progress report was conducted using an elemental mercury catalyst oxidation pilot unit (8000 acfm of flue gas treated) located at CPS' Spruce Plant in San Antonio, Texas. The pilot unit has four separate compartments that allow four different catalysts to treat flue gas from downstream of the host plant's particulate control device and upstream of its FGD system. Details of the pilot unit design, construction, catalyst preparation and pilot unit operation have been discussed in previous quarterly technical progress reports[1,2, 3, 4].

The activity of these catalysts is being determined by measuring the change in elemental mercury concentration across each catalyst, while ensuring that the total mercury concentrations do not change significantly across the catalyst. These measurements are primarily being conducted using a mercury semi-continuous emissions monitor (SCEM) developed with funding from EPRI. The analyzer has been described in a previous report[5]. Periodically, the analyzer results are being verified by conducting manual flue gas sampling efforts in parallel across each catalyst chamber by the Ontario Hydro method.

RESULTS AND DISCUSSION

This section provides details of technical results for the current reporting period, January 1 through March 31, 2005. The technical results discussed are from operation of the second pilot unit at CPS' Spruce Plant.

Pilot Unit Operation at Spruce Plant

Background

The pilot unit was started up at Spruce Plant in late August 2003 and operated with the Pd #1 and gold (Au) catalysts installed for most of the month of September. The host unit came off line for a fall outage the evening of September 26, and the outage continued until October 27, 2003. The two remaining catalysts (SCR and C #6) were installed in the pilot unit and the pilot unit was restarted on November 13, 2003. The unit has operated continuously with all four catalysts on line since then, except for periods of host plant outages. The only extended outage during that time period has been a recent outage from mid-February through mid-March of 2005.

Pilot unit inlet and catalyst outlet mercury concentration data were first collected for all four catalysts at Spruce the week of December 8, 2003. SCEM relative accuracy tests by the Ontario Hydro Method were conducted at the same time. The week of January 5, 2004, two SCEMs were taken to the site and used to measure flue gas total mercury and elemental mercury concentrations at the fabric filter inlet and outlet, and at the wet FGD outlet locations on the host unit. These measurements were made to develop a baseline characterization of host unit flue gas mercury conditions prior to rebagging the fabric filter with new bags. The rebagging began on January 12, 2004. Routine catalyst activity measurements by Hg SCEM were made on February 13, 2004, after 11 of the 14 compartments in the west fabric filter (directly upstream of the catalyst pilot unit) had been rebagged. The rebagging was completed at the end of February 2004. Subsequent catalyst activity measurements were made in made in May and August 2004. During October 2004, catalyst activity measurements were made across all four catalysts by mercury SCEM and by the Ontario Hydro Method. One catalyst activity measurement trip was conducted during the current quarter, with measurements by mercury SCEM.

Catalyst Pressure Drop Results

The pressure drop across the four catalyst chambers at Spruce remained nearly constant below 1 in. H_2O during the current quarter. It does not appear that sonic horns will be required to prevent fly ash buildup, most likely because a high-efficiency reverse-gas fabric filter is used for particulate control at this site. The use of a fabric filter results in a low dust loading in the pilot unit inlet flue gas, and a dust loading that has less residual electrostatic charge than would flue gas downstream of an ESP.

Catalyst Activity Results

One catalyst measurement trip was conducted during the quarter, in February 2005. Measurements were made February 3rd and 4th, then again on February 7th through 10th. In general, these results showed that the fabric filter outlet flue gas mercury content is highly oxidized, greater than 90% in some instances. This results in relatively low inlet elemental mercury concentrations to the pilot unit, often 1 $\mu g/Nm^3$ or less.

The low inlet elemental mercury concentrations and significant temporal variations in total and elemental mercury concentration make it difficult to quantify catalyst oxidation activity. To improve the accuracy of the mercury oxidation measurements, two newer mercury SCEMs with more sensitive atomic absorption detectors were used to simultaneously monitor the pilot inlet and catalyst outlet locations. In spite of this measurement approach, the results from this trip were inconclusive with regards to oxidation catalyst activity for the four catalysts. In some cases, catalyst outlet total and/or elemental mercury concentrations were measured to be higher than inlet concentrations, which is not an expected result.

In view of these results, a number of quality control/quality assurance measures were implemented, in addition to routine analyzer calibrations and mercury spike recovery measurements. Additional measures included replacing a suspect mercury SCEM with a third unit, switching SCEM units between analyzing the catalyst inlet and catalyst outlet gas locations, and using permanently installed versus temporary sample delivery piping and inertial gas separator (IGS) filters.

None of these efforts conclusively improved the apparent quality of the measured mercury concentration data. For example, in some instances the two SCEMs were used to analyze the same species (total or elemental mercury) in flue gas from the same location (e.g., catalyst pilot inlet). In some cases the results from the two analyzers agreed well, but in other instances there was a significant bias between to two analyzers' results. No consistent bias could be identified between the SCEMs in service or the sample conditioning and delivery systems, though.

Because of these measurement anomalies, the data from the February trip are still being reviewed and are not being presented in this report. A follow up measurement trip is being conducted in April. Additional quality control measures are being implemented for the April measurements.

Results from the April trip, and any reportable data from the February measurements will be included in the next Technical Progress Report. It is hoped that the April results will provide a good measure of the final catalyst activity at Spruce after 16 to 17 months of service in flue gas. In situ catalyst regeneration tests are also planned during the April trip.

CONCLUSION

At the Spruce site, the fabric filter upstream of the pilot unit has had two implications on the pilot testing. One is that is does not appear that sonic horns are required to keep fly ash from accumulating within the catalyst cells. The other implication is that the fabric filter oxidizes a high percentage of the elemental mercury in the air heater outlet flue gas, so the inlet gas to the pilot unit contains relatively low elemental mercury concentrations (typically <1 to 4 $\mu g/Nm^3$). This makes evaluation of catalyst performance difficult, as it is difficult to quantify flue gas elemental mercury concentrations that are well below 1 $\mu g/Nm^3$.

No new catalyst activity measurement results became available during the quarter, in spite of a measurement trip being made to Spruce in February. Many of the February SCEM results appear to be anomalous, and are being further reviewed rather than being reported herein. Consequently, no new conclusions can currently be made regarding catalyst performance in the flue gas downstream of the reverse-gas fabric filter at Spruce Plant.

REFERENCES

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